

Interface hole-doping in cuprate-titanate superlattices

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The electronic structure of interfaces between $\text{YBa}_2\text{Cu}_3\text{O}_6$ and SrTiO_3 is studied using local spin density approximation (LSDA) with intra-atomic Coulomb repulsion (LSDA+U). We find a metallic state in cuprate/titanate heterostructures with the hole carriers concentrated substantially in the CuO_2 -layers and in the first interface TiO_2 and SrO planes. This effective interface doping appears due to the polarity of interfaces, caused by the first incomplete copper oxide unit cell. Interface-induced high pre-doping of CuO_2 -layers is a key mechanism controlling the superconducting properties in engineered field-effect devices realized on the basis of cuprate/titanate superlattices.

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In complex thin-film oxide heterostructures of structurally compatible but physically dissimilar compounds, interface phenomena can substantially affect the charge properties. A prominent example [1] is the titanate superlattice composed of insulating layers of SrTiO_3 and LaTiO_3 , where the mixed valence (+3/+4) of Ti leads to an interface-driven electronic redistribution and to metallic conductivity. Moreover, when one of the superlattice compounds is a copper oxide film, where the high- T_c properties can be tuned by doping, the behavior is even more intriguing. Such heterostructures consisting of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -films grown on SrTiO_3 -layers are of essential importance due to their applications in superconducting field effect devices [2]. It is well established that external electrostatic fields can significantly affect the superconducting transition temperature (T_c) in these layered materials which is often understood in terms of electrostatic doping [the more charge is field-injected into the film the larger T_c] [2, 3]. Despite capturing the key mechanism of charge modulation in the field-effect, this concept does not include a detailed consideration of the microstructure of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -film near the interface assuming that the latter remains unaffected by the adjacent SrTiO_3 interface layer.

Several experimental facts, however, indicate an interface-related change of the electronic states in the cuprate/perovskite oxide heterostructures. First, recent experimental studies performed on the underdoped cuprate films resulted in a T_c -shift of about 5–15 K, whereas in the overdoped films no shifts were observed, a fact, which cannot be explained satisfactorily by field-doping [2]. Furthermore, studies of hole mobility in the CuO_2 planes of SrTiO_3 -cuprate superlattices suggest a substantial localization of injected holes even above the hole-density level necessary for a bulk superconductor-insulator transition [4, 5]. However, little is known about the electronic properties of the interfaces between the copper and titanium oxides. This is even more surprising considering the fact that despite the different physical properties, the structural compatibility of the cubic SrTiO_3 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ makes them good candidates

to assemble heterostructures and study interfacial phenomena. The electronic band insulating state of bulk SrTiO_3 with a wide gap of about 3 eV between the valence O 2p band and empty Ti 3d bands is reasonably well described within an LSDA approach. In contrast, the standard band theory calculations fail to describe the antiferromagnetic Mott insulating state of strongly underdoped or undoped cuprates like $\text{YBa}_2\text{Cu}_3\text{O}_6$. Instead, the band properties of $\text{YBa}_2\text{Cu}_3\text{O}_6$ with a gap of about 1.5 eV determined by Cu 3d and oxygen 2p electrons can be satisfactorily treated by introducing the intra-atomic orbital dependent Coulomb repulsion for the electrons in Cu 3d orbitals.

To provide deeper insight into the interface physics of such heterostructures, we present and interpret results of electronic structure calculations for the superlattice based on insulating $\text{YBa}_2\text{Cu}_3\text{O}_6$ -films and SrTiO_3 . As SrTiO_3 consists of an alternating sequence of electrostatically neutral (001) layers, one can expect that in such heterostructures, the chemical bonding at the (001) interface with $\text{YBa}_2\text{Cu}_3\text{O}_6$ will be determined by the first termination layer which can be either SrO or TiO_2 . It is worth pointing out that if the first unit cell of a $\text{YBa}_2\text{Cu}_3\text{O}_6$ -film were completely grown on the surface of SrTiO_3 , the interface would be electrostatically neutral. In this case, the direct influence of the interface would be essentially reduced to the small change in the band structure of $\text{YBa}_2\text{Cu}_3\text{O}_6$, originating from the mismatch of the lattice constants ($a = 3.9 \text{ \AA}$ in cubic SrTiO_3 versus $a = 3.86 \text{ \AA}$ in $\text{YBa}_2\text{Cu}_3\text{O}_6$). However, the recent X-ray studies of interface arrangement [6, 7] show clear indications of the incompletely growing unit cells of cuprate films at the SrTiO_3 substrate, which may drastically change the interface electronic properties.

In this case the interface between polar layers, formed with the anisotropic $\text{YBa}_2\text{Cu}_3\text{O}_6$ -crystal structure, and non-polar SrTiO_3 (001) planes would result in the so called “polar catastrophe” which appears on account of the divergent electrical potential [8]. The electronic compensation of the divergence can be achieved by a redistribution of the extra charge carriers near the inter-

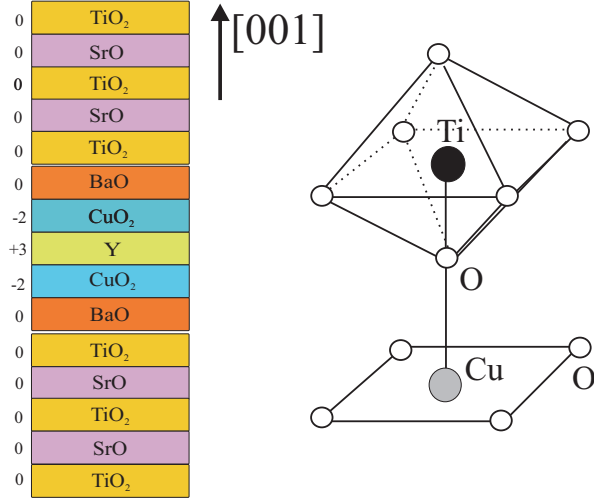


FIG. 1: Scheme of a YBaCuO/SrTiO₃-sandwich where the polar interfaces appear due to the incomplete Ba₂Cu₂O₆-unit cell with an interface structural configuration shown in detail on the right panel.

face which leads to a dramatical change of the electronic states in such a heterostructure. The possibility of such an electronic reconstruction has been demonstrated by Hesper *et al.* for a polar (111) surface of K₃C₆₀ [9].

To illustrate the resulting electronic properties, we consider first a superlattice formed on the basis of a sandwich-type supercell. The YBaCuO/SrTiO₃-supercell shown in Fig. 1 consists of an incomplete copper oxide unit cell YBa₂Cu₂O₆ shared between two layers, each containing 2 unit cells of SrTiO₃. Effectively, the interface bonding here appears by a ‘substitution’ of the CuO chains, terminating a full YBa₂Cu₃O_{7- δ} cell, with the TiO₂-planes which is illustrated in the right panel of Fig. 1. Our choice of interface bonding is strongly motivated by recent TEM-studies of the YBa₂Cu₃O_{7- δ} films and similar compounds grown on SrTiO₃ with pulsed laser deposition technique [6]. In the case, when the substrate of SrTiO₃ is terminated by a TiO₂-layer, the determined interface bonding arrangement is typically a stack of .../SrO/TiO₂/BaO/CuO₂/Y/CuO₂/BaO/CuO/... layers. Such structural stacks suggest an interface chemical bonding Ti-O-Cu with the oxygen of the BaO-layers shared between the CuO₂ and TiO₂-planes. From the electrostatical point of view, the initial ‘bulk-type’ electronic charging of the constituent layers indicated in the left panel of Fig. 1 would result in 1 extra hole which is needed in order to compensate the polarity. From the point of view of symmetry, this compensation leads to a doping of each block .../SrO/TiO₂/BaO/CuO₂ by 0.5 hole.

To understand the redistribution of the extra charge density, which would appear near the interface, we calculated the densities of states of a YBa₂Cu₂O₆/SrTiO₃

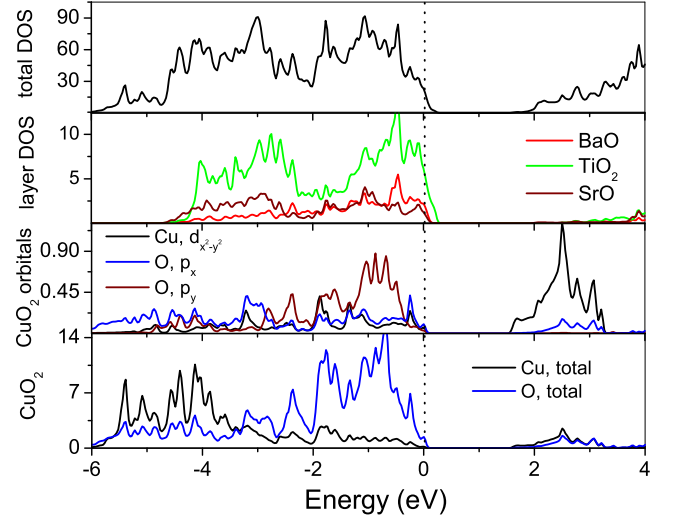


FIG. 2: Density of states of the SrTiO₃/YBa₂Cu₂O₆/SrTiO₃-sandwich calculated within LSDA+*U* approach with *U* = 8 eV and *J* = 0.8 eV for the electrons in Cu 3*d* orbitals. The zero of energy is at Fermi level.

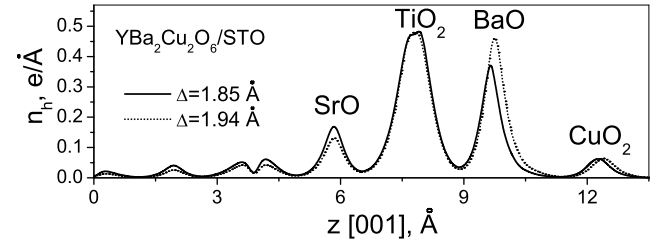


FIG. 3: Hole density distribution near the YBa₂Cu₂O₆/SrTiO₃-interface for optimized ($\Delta = 1.85$ Å) and unrelaxed ($\Delta = 1.94$ Å) cases. The position $z = 0$ is at bottom TiO₂-plane of SrTiO₃/YBa₂Cu₂O₆/SrTiO₃-sandwich.

sandwich using the linearized augmented plane wave method (LAPW) implemented in the WIEN2k package [10]. Technical details include the SIC-variant of the LSDA+*U* method [11] on a $9 \times 9 \times 1$ *k*-point grid with *U* = 8 eV and *J* = 0.8 eV on the Cu 3*d* orbitals. The lattice constants $a = b = 3.8984$ Å are fixed to the structural values of SrTiO₃, whereas the optimized interface distance $\Delta = 1.85$ Å between the apical oxygens of BaO layers and TiO₂ planes has been found by minimization of the total energy, which corresponds to $c = 27.53$ Å.

Fig. 2 shows the calculated density of states where the position of the Fermi level E_F is indicated by dots. One can immediately identify the metallic state with hole carriers in the superlattice from the total density of states as originating from the oxygen *p* states. We note that, similar to bulk YBa₂Cu₂O₆, the Cu $d_{x^2-y^2}$ states are empty and separated by a gap of 1.34 eV from oxygen 2*p* whereas Cu $d_{3z^2-r^2}$ and t_{2g} bands remain below the Fermi level. As one can see from Fig. 2, a substan-

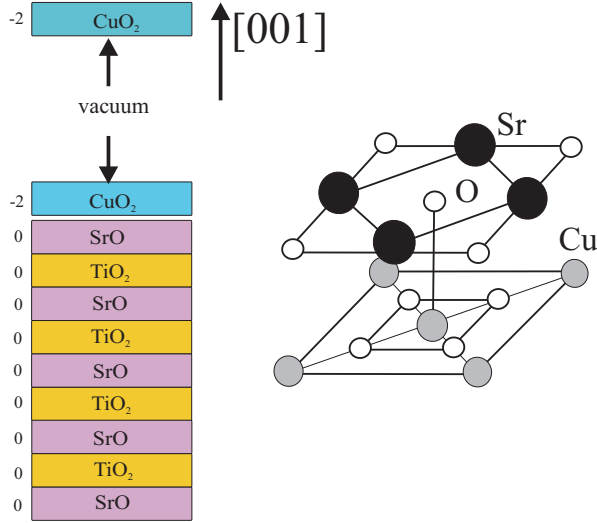


FIG. 4: Scheme of a polar $\text{CuO}_2/\text{SrTiO}_3$ -superlattice where a STO-layer is terminated by a SrO-plane. The right panel shows a structural configuration which appears at the interface.

tial amount of charge compensating hole density is distributed over CuO_2 planes. However, we find that also BaO layers as well as the first interface TiO_2 and SrO planes are doped. The upper boundaries of the O p bands of the more distant SrO and TiO_2 planes (with respect to the interface) remain almost on the same level with E_F which implies that the charge is confined essentially in the interface block of SrO/ TiO_2 /BaO/ CuO_2 layers. Fig. 3 shows the distribution of hole density spatially resolved along z ($[001]$)-direction within this interface block and calculated for optimized ($\Delta = 1.85 \text{ \AA}$) and unrelaxed ($\Delta = 1.94 \text{ \AA}$) sandwiches. To obtain this quantity, we have generated the charge density in the energy interval between the Fermi level and the top of the valence band. Specifically, we obtain that, although approximately 5% of the hole density is located in the CuO_2 planes, the major part is concentrated within the BaO ($\approx 25\%$) and the first TiO_2 (48%) and SrO (12%) layers. This suggests a finite metallic conductivity in the titanate, BaO and copper oxide planes. Furthermore, while the relaxation of the structure leads to the reduction of the hole density in the BaO plane and to its redistribution within the interface SrO and more distant planes, the hole density in the CuO_2 planes remains almost unaffected.

The resultant hole charge in the copper oxide planes of cuprate/titanate heterostructures clearly demonstrates that, apart from chemical doping, the interface polarity is another important mechanism which modulates the doping level in the cuprate films. In superconducting field effect devices, operated by electrostatic charging, an initial pre-doped hole density, caused by the interface, may have striking consequences on their performance. The most important feature is the T_c shift which may be di-

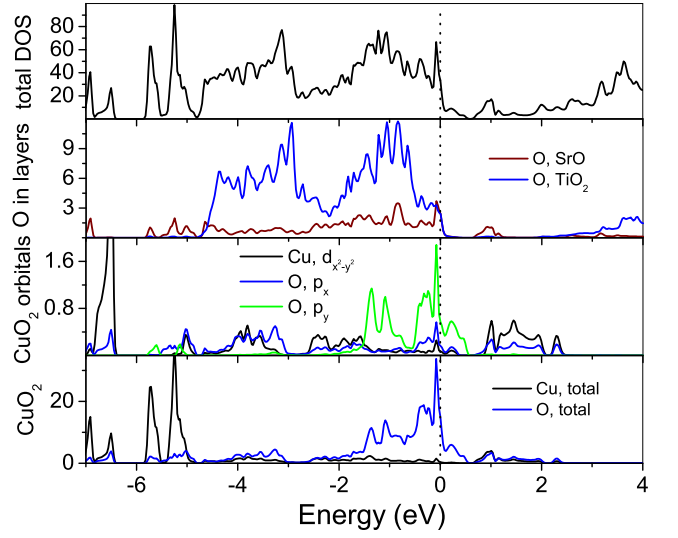


FIG. 5: Density of states of the superlattice with CuO_2 deposited on SrTiO_3 , terminated by SrO (LSDA+ U studies). The zero of energy is at Fermi level.

rectly affected when a typically achievable hole density ~ 0.05 is injected into the already pre-doped ($x = 0.025$) copper oxide film. Moreover, it appears that much higher hole doping levels including strong overdoping at the interfaces can be obtained in other interface configurations when the first unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at the interface remains incomplete.

To demonstrate such a structurally induced overdoping, we consider a case in which a copper oxide plane is directly deposited on a SrTiO_3 substrate terminated by SrO (Fig. 4). The direct deposition of the single $\text{Cu}^{2+}\text{O}_2^{4-}$ plane on the non-polar titanate layer would require 2 extra holes to maintain the overall charge neutrality. To achieve such an extremely high doping level, interface electronic reconstruction is inevitably required. The importance of electronic reconstruction is strongly supported by significant smoothing of interference fringes observed with anomalous X-ray scattering in doped $\text{La}_2\text{CuO}_{4+\delta}$ -films—an effect explained by the mobile carrier depletion in cuprate films near the SrTiO_3 substrate [7]. Apart from the electronic mechanism, other forms of interface reconstruction could modify the chemical composition. For example, the ionic compensation due to the cation intermixing and oxygen vacancies (oxygen missing in CuO_2 during the growth) will be a competing mechanism to compensate the polarity [8]. However, it is still instructive to enforce atomically flat and stoichiometric surfaces in order to investigate comprehensively the electronic mechanism [12].

In our theoretical studies, in order to focus on the effect of electronic reconstruction, we have introduced a decoupling vacuum layer of 13 \AA thickness between the CuO_2 surfaces in the superlattice of the same slab ge-

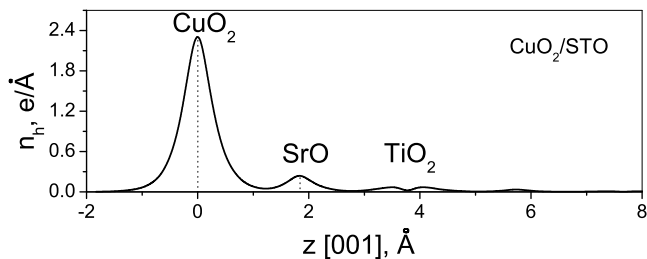


FIG. 6: Hole density distribution in the interface planes of the $\text{CuO}_2/\text{SrTiO}_3$ superlattice. Here $z = 0$ corresponds to the location of the lower CuO_2 -plane.

ometry, as shown in Fig. 4. Furthermore, we have optimized the superlattice structure with a relaxed distance $\Delta = 1.83 \text{ \AA}$ between the interface CuO_2 and SrO which corresponds to a total energy minimum. The electronic density of states calculated from LSDA+ U is shown in Fig. 5. Here we see that the effect of hole doping is more pronounced than in the case of the $\text{YBa}_2\text{Cu}_2\text{O}_6/\text{SrTiO}_3$ sandwich: the energy gap between O p and Cu d states basically disappears and the Fermi level is located well below the top of the valence band which characterizes a metallic state with hole carriers. The hole charge is present in the CuO_2 planes, where it is hybridized between the oxygen p_x and p_y , and Cu d orbitals. Also, there is clear evidence for holes in the first SrO layer and in the next TiO_2 layer of SrTiO_3 . In these layers, E_F is also located below the top of the O p bands.

How is the hole charge redistributed near the interface? To provide more details, we have calculated the density of holes in the planes nearest to the interface. The results in Fig. 6 show that most of the charge (about 80%) is confined to the CuO_2 plane and a substantial amount of hole density is located in the first SrO plane (about 11%) and more distant TiO_2 (8%) plane. Consequently, such heavy overdoping of CuO_2 should completely exclude any possibility for superconducting state in the interface unit cells of the cuprate films.

As the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is closely compatible with the perovskite SrTiO_3 , all possible basic polar interface configurations can be effectively reduced to the discussed two cases. In the first case (A) with TiO_2 -termination of SrTiO_3 , the first interface layer in the incomplete cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is expected to be BaO in order not to disturb the perovskite stacking. In the second case (B) with SrO termination of SrTiO_3 , the CuO_2 layer is the most compatible for a continuous stacking (cf. Fig. 4). In both of these situations, the interface polarity leads to a hole density in CuO_2 ranging from ~ 0.05 (case (A)) to ~ 1.6 (case (B)) holes per interface. In addition, due to steps and different stacking modes at the interfaces [6], one expects rather a combination of cases (A) and (B). In fact, the latter implies the formation of weak links with either connected or discon-

nected underdoped and heavily-overdoped regions. For such possible interface configurations, the direct consequence of the deduced pre-doping is a strong suppression of the T_c shift related to the hole injection—or even a complete suppression of the superconductivity in few unit cells of the cuprate films.

Up to now, the growth of high-quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -films terminated by complete unit cells remains to be a challenging task due to their roughness caused by ionic compensation of the interface polarities. In order to make a step towards perfect interfaces, where the hole injection would completely determine the superconducting dome, we need to consider other superconducting cuprates as possible candidates for non-polar interface. In this context, a proposal for field effect experiments is to grow $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (SCOC) or $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (CCOC) on SrTiO_3 . These systems can be perfectly cleaved between $\text{SrCl}(\text{CaCl})$ layers, and the deposition on SrTiO_3 terminated by TiO_2 would result in a nonpolar interface stack $\dots \text{TiO}_2/\text{SrCl}/\text{CuO}_2/\text{SrCl}/\text{SrCl}/\dots$ (for CCOC a similar stack with $\text{Ca} \rightarrow \text{Sr}$). Our LSDA-calculations for such superlattices suggest an insulating state. The lattice constants' mismatch ($a = b = 3.96 \text{ \AA}$ in SCOC) results in a slight increase ($V_{pd}/V_{pd}^{\text{bulk}} = 1.074$) of the p - d hybridization integral V_{pd} [13]. Assuming the on-site Hubbard coupling not to be affected by strains, the direct interface effect in SCOC/ SrTiO_3 is a renormalization of the parameters of the effective t - J model [14] ($t/t_{\text{bulk}} = 1.15$, $J/J_{\text{bulk}} = 1.33$) which would only increase T_c , without changing the doping level. Such superlattices, where the combination of chemical doping by Na and electrostatic hole injection should not be affected by the interface pre-doping, would be ideal candidates to probe the electrostatic field effect.

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